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The effect of various chemical treatments on the pyrolytic pattern of peat humic acid

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ABSTRACT

The present study describes the pyrolytic patterns of a series of humic preparations obtained from a peat humic acid subjected to chemical modifications, such as methylation, oximation, sulphonation, nitration, amidation, ammonia fixation, acetylation, acid and alkaline hydrolysis, hydrogen peroxide treatment, etc.

Some diagnostic pyrolysis compounds were found which can be useful in studying N speciation in humic substances. In addition, the noticeable differences in the distribution patterns of the alkyl series released upon pyrolysis were interpreted in terms of the changes introduced in the structural arrangement of the humic macromolecules.

Chemical treatments; derivatization; humic acids; peat; pyrolysis.

INTRODUCTION

Both classic and recent studies have exploited the possibilities of transforming humic acids (HAs) (the alkali-soluble, acid-insoluble colloidal fraction from soil humus and fossil organic sediments) into modified products suitable for agronomic and industrial applications [1–4].

Amongst the different experimental approaches, analytical pyrolysis can be suitable for monitoring the extent to which the HAs are transformed by the various treatments [5,6].

Owing to the complex and variable composition of the humic acids, the possibilities of obtaining precise structural information from their pyrolysis patterns are greatly limited. In practice, the structural information gained by analytical pyrolysis is often restricted to the detection of some source

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indicator compounds or the quantitative determination of broad groups of pyrolysis products with a common origin.

In addition, when considering that only a limited portion of the HA is transformed into volatile products (the stable residue can amount to about 50% of the original material), it is probable that the yield of pyrolysis compounds will depend more on the macromolecular conformation of the HA — the speciation of the different units — than on its whole quantitative composition.

This can be the cause of the frequent observation that humic materials from varied sources often lead to similar pyrolysis patterns, whereas the opposite has been reported in other cases.

In the present research the pyrolysis patterns are compared for a variety of colloidal humic preparations with potential agronomic or industrial applications. Special attention is given to the introduction of specific changes in the functionality of the humic macromolecule. The individual pyrolysis products are expected to reflect the effect of the derivatizations of the pre-existent functional groups, the incorporation of heteroatoms and the concomitant changes in the nature of the different intramolecular interactions affecting the structural arrangement of the HA units.

MATERIALS AND METHODS

Materials

The original HA was extracted from sapric peat from Vivero (Lugo, Northern Spain) [7] with 0.5 mol l^{-1} potassium hydroxide in a 50 l reactor at room temperature. After sedimentation, the supernatant solution was centrifuged and the HA was precipitated with hydrochloric acid. The precipitate was washed with water to remove any chlorides and then desiccated at 60°C. A portion of this material was separated as a reference sample (REF), and the remaining material was divided into eleven 40 g portions and subjected to the treatments listed below.

Owing to the practical applications of transformed HAs used in the present study, no attempt was made to perform the extraction and chemical modifications under the optimum exhaustive conditions usual in standard laboratory studies: the conditions used were more representative of low-cost industrial processes.

Sample ACE is the acetylated preparation obtained by heating the HA with 300 ml of acetic anhydride at 95°C for 24 h [8]. The organic fraction soluble in acetic anhydride was precipitated with water and aggregated to the acetylated product.

Sample ALK corresponds to the residue after alkaline hydrolysis. The HA was heated under reflux with 100 ml of 1 mol l^{-1} potassium hydroxide for 12 h, precipitated with hydrochloric acid and washed with water.

The so-called "ammonia fixation" is a classical treatment for lignocellulosic products [9]. Sample AMO was obtained by treatment with 50 ml of 30% aqueous NH_3 at 95°C in a screw-stoppered Pyrex flask for 5 h.

Sample AMI is the amidated preparation obtained by adding 300 ml methanol, 80 ml water and 320 g diethylamine to the HA, which was heated for 12 h under reflux. The solvents were distilled and the sample was washed with methanol [10].

Sample HID corresponds to the hydrolysis residue after boiling the HA with 300 ml of 6 mol l^{-1} hydrochloric acid for 6 h (four times). This classical treatment led to some decarboxylation of the HA, yielding substantial amounts of carbohydrate, protein, and some phenolic compounds [11].

Sample LIP included 5% loosely-attached stearic acid: the mixture of potassium humate and potassium stearate obtained by adding 0.1 mol l^{-1} potassium hydroxide to the mixture was precipitated with hydrochloric acid and washed with water.

Sample MET is the methylated product obtained by treating a methanol suspension of the HA with 40 ml of ethereal diazomethane [12]. The reaction was carried out in a 500 ml screw-stoppered flask for 24 h. The residual diazomethane was destroyed by air and sunlight exposure, the residual ethyl ether was evaporated and the treatment was repeated three times.

Sample NIT is the nitrohumic acid prepared by treating the HA in an ice bath with 100 ml of 50% (v/v) nitric acid. After 24 h the mixture was heated under reflux at 95°C for 30 min [1]. The precipitate was dialyzed.

In order to obtain sample OXI, the original HA, suspended in 200 ml of pyridine, was oximated with 150 g hydroxylammonium chloride and refluxed for 24 h [10]. The product was dialyzed.

Sample PER was obtained after treating the original HA, dissolved in 100 ml of 0.1 mol l^{-1} potassium hydroxide, with 20 ml hydrogen peroxide in water (30% wt.) at 60°C for 4 h.

Sample SUL was obtained by sulphonating the HA with 150 ml of 65% sulphuric anhydride and 150 ml sulphuric acid. The mixture was cooled at intervals in an ice bath to prevent excessive foam formation. After the sulphonation reagent was added, the mixture was heated at 80°C for 1 h. The reaction was stopped by the addition of water and the precipitate was recovered by centrifugation and washed with water.

Some spectroscopic characteristics of the derivatized or transformed humic preparations and of the sample REF are reported elsewhere [13].

Pyrolysis procedure

Analytical pyrolysis was carried out at 700°C at a rate of 20°C ms^{-1} in a CDS Pyroprobe 190 unit equipped with a Pt-coil heater. Samples of 3 mg in a quartz tube were pyrolyzed under an He atmosphere and the volatile products were condensed in a U tube (2 mm i.d.) submerged in liquid N_2. The operation was repeated eight times in the same tube and the pyrolysis

products were recovered with methylene chloride. They were then injected into a Hewlett-Packard 5730A gas chromatograph (FID detector) with an OV-101 column and into a Hewlett-Packard 5988A GC/MS system, for peak measurement and identification, respectively.

Using this off-line method, average representative chromatograms are obtained, column contamination with tars is considerably reduced and no substantial loss of information occurs, due to the meaningless character of the very low MW products lost in these conditions.

RESULTS AND DISCUSSION

Non-alkyl pyrolysis products

Table 1 and Fig. 1 show the pyrolysis products other than alkyl compounds. In general, phenol was the most abundant compound in addition to different kinds of alkyl phenols conforming to the structures described from the pyrolytic fragmentation of altered lignin polymers [14]. This reveals substantial input from vascular plants to the formation processes of the HAs in the peat studied.

Some molecules that were characteristic of the derivatized samples were found. The treatments incorporating N into the HA can be readily differentiated by means of their pyrolysis compounds: the formation of diethyl formamide and diethyl acetamide was characteristic of the HA after amidation. On ammonia fixation, the HA yields alkyl pyrroles. Only methyl indene was found as a diagnostic compound after nitration: the large yield of alkanes and olefins was the most characteristic feature of the pyrogram from this sample. Both cyanoguaiacol and bipyridine were found as specific compounds for sample OXI. Other pyrolysis compounds conformed with the derivatization procedure used: alkyl sulphides were identified from the sulphonated sample.

Of particular importance was the series of prominent acetate peaks (base ion 43) in the pyrogram of sample ACE. Although there was no definitive identification by MS owing to the lack of molecular ions, these compounds showed fragmentation patterns similar to those of partially acetylated carbohydrate derivatives [15]. The presence of such peaks contrast with the lack, in this and other samples, of the typical pyrolysis products expected from native carbohydrates. In fact, the very low amount of sugars, which are traditionally yielded by the destructive methods applied to HAs, is often interpreted as being due to the negligible contribution of polysaccharide diagenesis in the humification pathways. Nevertheless, the possible presence of heavily altered anhydrosugar polymer structures has also been postulated, and the present results suggest that, with suitable derivatization treatments, analytical pyrolysis could be of interest in the study of the carbohydrate-derived structures of humic substances.

TABLE 1

Main pyrolysis products (other than alkyl compounds) of chemically transformed humic acids from sapric peat; peak area values relative to nonacosane (= 1000)[a]

No.	Compound	REF	ACE	ALK	AMI	AMO	HID	LIP	NIT	MET	OXI	PER	SUL
1	4-Hydroxy-4-methyl-2-pentanone	844	1483	865	377	352	973	1167	1807	194	2576	262	1667
2	2C-Alkyl pyrrole	0	0	0	0	310	0	0	0	0	0	0	0
3	*N*,*N*-Diethylformamide	0	0	0	2213	0	0	0	0	0	0	0	0
4	Dimethyltrisulphide	0	0	0	0	0	0	0	0	0	0	0	2556
5	Phenol	391	1224	692	1902	1831	554	1333	783	1165	203	879	3000
6	*N*,*N*-Diethylacetamide	0	0	0	1475	0	0	0	0	0	0	0	333
7	2-Methylphenol (*o*-cresol)	547	362	173	443	211	152	333	0	262	34	187	556
8	3-Methylphenol (*p*-cresol)	1484	897	577	508	732	518	417	0	437	102	682	1333
9	3-Methoxyphenol (guaiacol)	516	2276	933	1525	1915	679	2250	48	1262	288	1121	1778
10	2,4-Dimethylphenol	313	293	154	590	352	98	250	0	175	0	93	222
11	1-Methyl[1*H*]indene	0	0	0	0	0	0	0	96	0	0	0	0
12	2,6-Dimethylphenol	516	672	298	426	352	241	417	0	330	34	243	333
13	4-Ethylphenol	421	694	192	500	614	285	500	120	602	51	579	166
14	3-Methoxy-4-methylphenol (4-methylguaiacol)	672	552	365	279	873	446	917	0	340	51	430	556
15	1,2-Dihydroxybenzene (catechol)	781	759	385	705	366	438	500	0	175	169	402	667
16	Dimethyltetrasulphide	0	0	0	0	0	0	0	0	0	0	0	2667
17	4-Ethyl-2-methoxyphenol (4-ethylguaiacol)	1219	966	808	1033	1408	625	1417	96	515	51	794	667
18	4-Methyl-1,2-dihydroxyphenol (4-methylcatechol)	203	0	87	361	0	63	0	0	0	0	402	111
19	Methylnaphthalene	281	224	77	82	0	54	83	0	117	0	121	222
20	3-Methoxy-4-vinylphenol (4-vinylguaiacol)	359	259	519	361	451	214	1000	0	243	102	374	111
21	2,6-Dimethoxyphenol (syringol)	656	845	510	623	704	339	500	0	369	51	467	0
22	4-Ethyl-1,2-dihydroxybenzene (4-ethylcatechol) + *C*2-naphthalene	281	69	29	66	141	18	0	0	0	0	187	0
23	4-Hydroxy-3-methoxybenzonitrile (4-cyanoguaiacol) + 2,2'-bipyridine	0	0	0	0	0	0	0	0	0	203	0	0
24	1-(4-Hydroxy-3-methoxyphenyl)ethanone (acetoguaiacone)	250	328	317	459	338	205	500	0	272	68	346	111
25	4-Hydroxy-3-methoxybenzoic acid, methyl ester (methyl vanillate)	0	0	0	0	0	0	0	0	340	0	0	0
26	1-(4-Hydroxy-3-methoxyphenol)-2-propanone (guaiacylacetone)	156	0	77	131	197	89	167	0	0	17	121	0
27	4-Hydroxy-3-methoxybenzoic acid (vanillic acid)	313	310	38	164	127	71	0	0	136	0	785	0
28	1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone (acetosyringone)	281	627	307	295	428	250	291	96	97	101	345	166
29	1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (propiosyringone)	312	440	298	139	400	321	500	0	194	84	121	71

[a] REF = original peat humic acid, ACE = acetylation, ALK = alkaline hydrolysis, AMO = ammonia fixation, AMI = amidation, HID = acid hydrolysis, LIP = "fixation" of the n-C_{18} fatty acid, MET = methylation, NIT = nitration, OXI = oximation, PER = H_2O_2 oxidation, SUL = sulphonation.

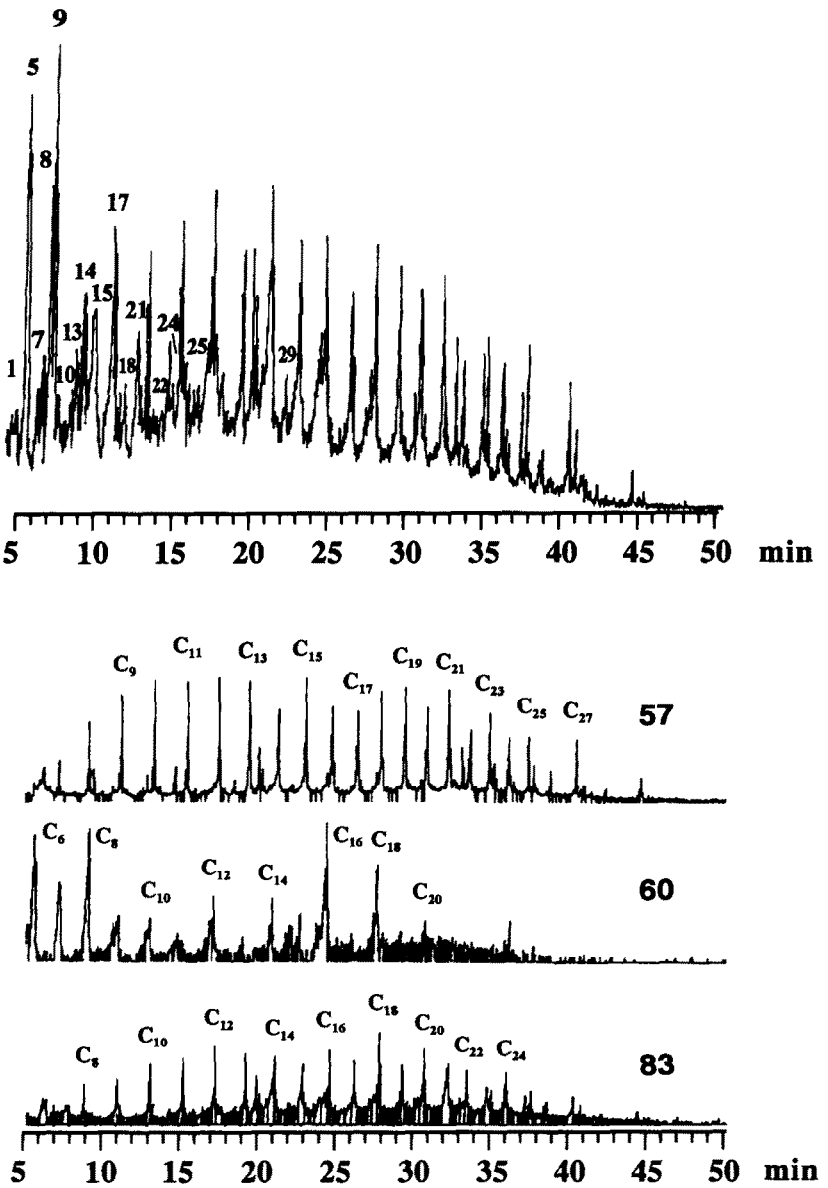

Fig. 1. Top: chromatographic separation (total ion chromatogram) of the pyrolysis products from a peat humic acid. Peak numbers correspond to those in Table 1. Below: traces corresponding to ions frequent in the main alkyl series (57 for alkanes, 60 for acids, 83 for olefins).

Finally, the typical degradation procedures (HID, ALK, PER) were not characterized by new types of diagnostic compounds, but by changes in the relative abundance of pyrolysis products.

The above results are summarized in the plot obtained after the principal component analysis of the data from the twelve humic preparations, defined

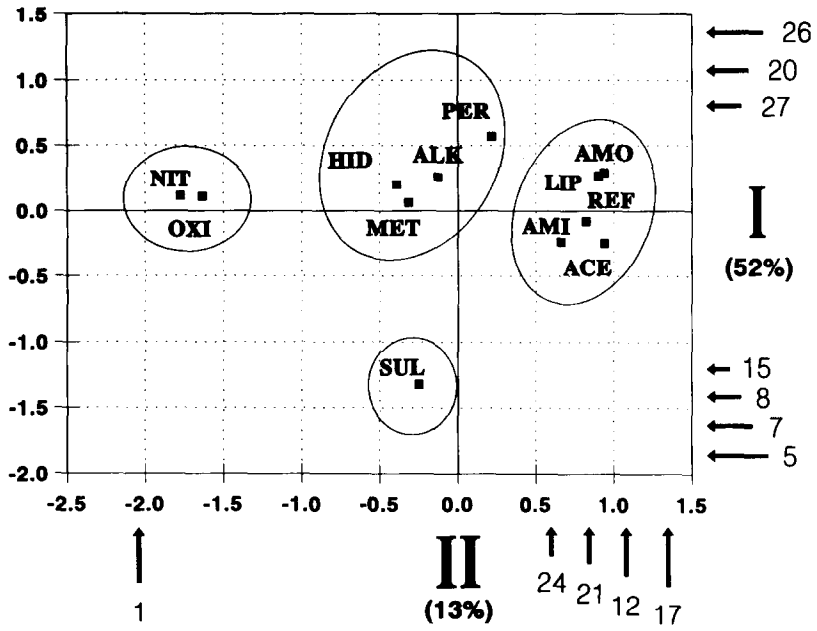

Fig. 2. In the space defined by the first two axes obtained after principal component analysis, representation of the values for the derivatized humic acid preparations subjected to analytical pyrolysis, and defined by the variables corresponding to the size of the chromatographic peaks 1, 5, 7–10, 12–15, 17, 20–22 24 and 26–29 (Table 1). The variables with the highest loading factors on the axes are indicated (% variance explained = 65%). REF = original peat humic acid, ACE = acetylation, ALK = alkaline hydrolysis, AMO = ammonia fixation, AMI = amidation, HID = acid hydrolysis, LIP = "fixation" of the n-C_{18} fatty acid, MET = methylation, NIT = nitration, OXI = oximation, PER = H_2O_2 oxidation, SUL = sulphonation.

by the variables corresponding to the size of the most frequent peaks in the chromatograms (other than alkyl compounds), indicated in the caption of Fig. 2. This plot showed that, when compared with sample REF, the preparations NIT and OXI showed the greatest changes in the pyrolytic patterns. The probable cleavage of intramolecular bridges, which in these cases affect the preferential disruption of interactions with alkyl constituents (see below), resulted mainly in the enhancement of peak No. 1 (a carbohydrate-derived cyclic ketone).

Other samples (ACE, AMI, AMO and LIP) showed high values for axis I, and the greatest proximity to sample REF. Such preparations may have a neat substitution of reactive surfaces in common, with no great changes in the molecular arrangement. The information concerning the respective differences in their pyrolysis patterns is reflected in axis II: in particular, the samples showing negative values tend to yield simple pyrolysis compounds (phenol, cresols, . . .), as opposed to the most characteristic lignin-derived products common in samples with positive values for this axis.

The central region of the plot is occupied by points corresponding to samples subjected to relatively mild degradation procedures, in addition to sample MET. There is reason to assume that methylation, despite its non-destructive character, causes sufficient changes in the intramolecular interactions of the HA to yield relative abundances of pyrolysis products comparable with the former treatments.

Sample SUL behaved in a unique way upon pyrolysis: the patterns differed greatly from the other samples. The release of substantial amounts of phenols and cresols conforms to the results of non-destructive methods [13], which showed that sulphonation leads to a condensed heavily-degraded aromatic material.

When a non-linear multivariate approach was used (Euclidean distance and MDSCAL algorithm [16]) the point arrangements were qualitatively similar, but the values for samples NIT and OXI were extremely far from those for clusters formed by the remaining samples.

Alkyl series

The HA pyrograms showed conspicuous series of hydrocarbons (alkanes, alkenes and α, ω-alkadienes) and of fatty acids. Such compounds can be derived not only from the free or loosely-attached HA alkyl species — for a long time their presence has been suggested by the results of mild degradation methods — but also from the recalcitrant polymer material that contributes to the little-known alkyl structures frequently reported in most bio- and geopolymers [17,18].

Alkanes

A well-defined alkane series (ion 57) was obtained from all the humic preparations (Figs. 1 and 3).

In sample REF, the distribution series was bimodal: the C14–C29 range, with a maximum at C19 and a low even-to-odd C number ratio, is often considered to be derived from epicuticles of peat-forming higher plants [19]. However, the lowest MW chains ($<$C14, maximum at C11) showed no odd C number preference and may consist of those chains coming from pyrolytic fragmentations.

The most frequent change after the different treatments was the relative decrease of the lowest MW homologues (Fig. 3). Such a phenomenon is particularly marked in sample OXI, where the relative amounts of alkanes $<$C13 were negligible and a variety of long-chain branched alkanes ($>$C17) are released. A possible explanation is that the derivatization of quinone and some carboxyl groups caused the most effective loosening of the HA structure through the disappearance of intramolecular bridges, thus enhancing the release of the alkyl species in an uncontrolled fashion.

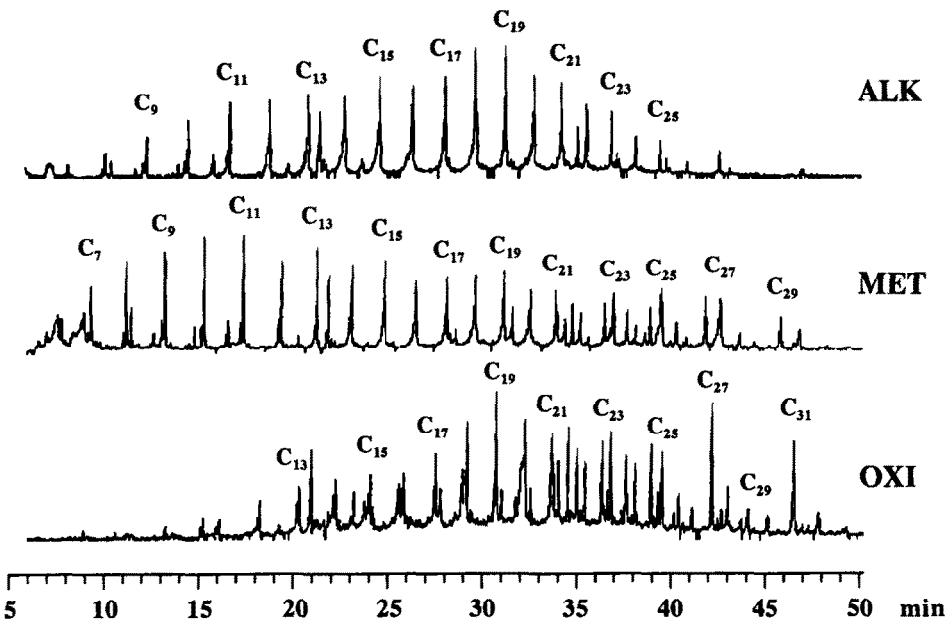

Fig. 3. Alkane series (ion 57) released by some humic acid preparations subjected to chemical transformations: ALK = alkaline hydrolysis, MET = methylation, OXI = oximation.

More intense changes were observed in sample MET (Fig. 3): methylation affected the partition phenomena within the internal HA surfaces, which favoured the early release of fatty acids >C18 in the form of methyl esters, as indicated below. The resulting alkane series showed the dominance of the lowest MW compounds, in addition to substantial amounts of long-chain (>C19) branched alkanes, the proportion of which was low in sample REF.

Finally, the smallest changes in alkane patterns was observed for sample AMO.

Alkenes

In contrast with the alkane series, the distribution patterns of olefins were, in general, unaffected by the different treatments. The series ranged from C6 to C28, with the maximum at C18 and a clear preference for the even C numbered chains (Fig. 1). Only three samples showed conspicuous deviation from this pattern. The most striking deviation corresponds to sample MET where, as opposed to alkanes, additional alkenes > C18 (maximum at C25) were released, including a variety of branched alkenes. The latter were also frequent in sample OXI, where the amount of the homologues <C13 was low. Only after sulphonation — the treatment causing the most effective removal of the aliphatic HA structures [10] — was a very poor alkene yield observed.

Fatty acid series

The fatty acid patterns (ion 60) were simple when compared to those of hydrocarbons (Fig. 1). In sample REF a clear dominance was observed for the even-numbered homologues, with high values for palmitic, stearic, myristic and lauric acids, but also for the C6–C10 acids, presumably formed by the pyrolytic breakdown of long-chain compounds. As expected, the LIP pyrogram showed a dominant peak for the C18 acid, suggesting that, in the case of the loosely-attached species, the pyrolysis patterns reflect the chain length of the unaltered material added.

The pattern remains relatively constant after most of the derivatizations. The greatest changes were observed in sample OXI (the almost exclusive presence of C16, C18 and C20 homologues) as opposed to sample NIT, where only the C5–C10 homologues were found.

In sample MET the series was very poor: from this sample the fatty acids were readily released as methyl esters (ion 74). The C16–C30 series of even-numbered methylated acids (not illustrated) reached its maximum at C26 and suggested the volatilization of unaltered molecules in loose association with the humic matrix.

CONCLUSION

As expected from the experimental design, some characteristic compounds were found after pyrolysis of the derivatized samples where N or S are incorporated in the HA.

The results also suggest that most of the alkanes released upon pyrolysis reflect the chain-length distribution of material physically attached to the HA. This is evident in the case of additional release after methylation of methyl esters of long-chain acids (C16–C30), maximum at C26), interpreted as the volatilization of unaltered fatty species, which are set free after transesterification and/or the loosening of the humic matrix owing to a decrease in hydrogen-bond-type intramolecular interactions. After oximation, analogous processes are probably responsible for the release of high amounts of branched and long-chain alkanes not obtained with other treatments.

The pyrolysis results confirmed that the probable selective loss of soluble nitroaromatic products after HA nitration leads to a condensed predominantly polyalkyl residue [10]. The fact that a conspicuous olefin pattern was obtained from this sample — where fatty acids > C8 were lacking — in addition to the constant olefin series in the samples showing drastic changes in their alkane and fatty acid series (OXI, SUL, . . .), suggests that the most stable and condensed HA polymethylene species are preferentially reflected by these pyrolysis products.

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